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MOLECULAR POLARIZABILITY AND ABSOLUTE RAMAN INTENSITIES OF Σ_g^+ MODES IN MERCURY DICYANIDE AND MEAN AMPLITUDES OF VIBRATION IN SOME LINEAR DICYANIDES

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ABSTRACT A brief survey of the vibrational and structural data has been made for mercury dicyanide, silver dicyanide ion and gold dicyanide ion possessing a linear symmetrical structure with the symmetry point group $D_{\infty h}$. Molecular polarizability has been computed for mercury dicyanide by the Lippincott-Stutman method from a semi-empirical delta-function model of chemical binding using a variational method and delta-function electronic wave functions. The calculated value of the molecular polarizability is in good agreement with the experimental one. The delta-function potential model has been used to obtain an expression for the derivative of the mean molecular polarizability with respect to a change in the internuclear distance at the equilibrium configuration for symmetrical stretching modes in the ground electronic state of a polyatomic system and applied to mercury dicyanide to obtain the polarizability derivatives for the symmetrical $C{\equiv}N$ and Hg–C stretching modes. Mean amplitudes of vibration have also been evaluated by the Cyvin method employing the symmetry coordinates at the temperatures $T = 298°K$ and $T = 500°K$.

INTRODUCTION

A linear dicyanide of $D_{\infty h}$ symmetry is one of the simplest and highly symmetrical molecules for which sufficient number of investigations on the nature of its chemical bonds has not been made. The Raman spectrum of mercury dicyanide was studied and the three Raman lines were assigned by Krishnamurti (1930), Woodward (1930), Petrikaln and Hochberg (1930), Braune and Engelbrecht (1931), Wolkenstein (1937), Francois (1939), Woodward and Owen (1959) and Mathieu (1959). The infrared absorption and Raman spectra of $Hg(CN)_2$, $KAu(CN)_2$ and $KAg(CN)_2$ were studied and the fundamentals assigned by Jones (1957, 1963, 1965). The experimental and theoretical investigations by Hassel (1926), Hanawolt, Rin and Frevel (1938), Zhdanov and Shugam (1944) Halfort (1946) and Hoard (1933) favour a linear symmetrical structur for mecury dicyanide, silver dicyanide ion and gold dicyanide ion. The fundamental frequencies in cm^{-1} and internuclear distances in Å for these three dicyanides are given in Table I. It is aimed here on the basis of these recent vibrational and structurel data to compute the molecular polarizabilty and absolute Raman intensities of Σ_g^+ modes in merdury dicyanide by the Lippincott and Stutman method (1964) employng the

delta-function model of chemical binding and evaluate the mean amplitudes of vibration for these three dicyanides by the Cyvin method (1959) employing the symmetry coordinates. The importance in undertaking such investigations is that the molecular polarizability, polarizability derivatives and mean amplitudes of vibration obtained here would be much useful for the interpretation of the results of 1) experimental refractive indices i.e. deriving the mean molecular polarizability from measured refractive index through the well-known Lorentz-Lorenz equation and making a comparison with a value obtained from the present study, 2) experimental absolute Raman intensities or polarizability derivatives and 3) electron diffraction studies.

MOLECULAR POLARIZABILITY

The polarizabilities for atoms and simple diatomic molecules were calculated by Hasse (1930, 1931), Hirschfelder (1935), Hylleraas (1930), Kirkwood (1932), Mrowka (1932), Steenshelt (1935), Buckingham (1937), Bell and Long (1950), Abbott and Bolton (1952, 1953) and Kolker and Karplus (1963) upon different wave functions given by Rosen (1931), Wang (1928) and Guillemin and Zener (1929) and a critical analysis was made by Van Vleck (1932) and Atanasoff (1930). The first use of a delta-function potential model was maze by Ruedenberg and Parr (1951) and Ruedenberg and Scherr (1953) Later, Frost (1954, 1955, 1956) applied a delta-function model of chemical binding to the calculation of energies of various systems with introduction of a branching condition and followed by Lippincott (1955, 1957) with a semi-empirical delta-function potential model. Lippincott and Dayhoff (1960) used the semi-empirical delta-function techniques in predicting vibrational frequencies, anharmonicities, bond dissociation energies and equilibrium internuclear distances. Recently, Lippincott and Stutman (1964) applied this semi-empirical model in generating component polarizabilities in order to compute the mean molecular polarizabilities for both diatomic and polyatomic molecules The same method has been adopted here for mercury dicyanide and one may refer to Lippincott and Stutman (1964) for the detailed theoritical considerations and calculations.

The delta-function strengths A's in atomic units, atomic polarizabilities α's in 10^{-25} cm^3 and c's in atomic units used here are as follows : $A_{Hg} = 0.322$, $A_C = 0.757$, $A_N = 0.927$, $\alpha_{Hg} = 178.05$, $\alpha_C = 13.7$, $\alpha_N = 7.43$, $c_{Hg} = 1.675$, $c_C = 3.028$ and $c_N = 4.146$ The molecular polarizability is composed mainly of bond parallel components and bond perpendicular components. The contribution to the bond parallel component by the bond region electrons is given as $\alpha_{\|b} = 4nA_{12}(1/a_0)(\langle x^2\rangle)^2$ where n is the bond order, A_{12} the root mean-square delta-function strengths of the two nuclei involved and $\langle x^2\rangle$ the mean-square position of a bonding electron expressed as $\langle x^2\rangle = (R^2/4) + (1/2c_{R_{12}})$ where R is the equilibrium internuclear distance and $c_{R_{12}}$ the root mean-square value of c_{R_1} and c_{R_2}. The calculated values of polarizability components in 10^{-25} cm^3

for the $C \equiv N$ and Hg—C bonds are 22.245 and 58.926 respectively. In the case that the bond is of heteronuclear type, a polarity correction is introduced using the Pauling's scale of electronegativities (1960) to determine the percent covalent character. The calculated value of the polarizability component for the Hg—C bond after introducing the polarity correction is 53.854×10^{-25} cm^3. Because of greater electronic distribution in the bond region, no polarity correction is introduced for the C ≡ N bond. The contribution by the nonbond region electrons to the parallel components of the total system is calculated from the remaining electrons in the valence shell of each atom not involved in bonding from the expression $\Sigma \alpha_{\|n} = \Sigma f_j \alpha_j$ where f_j is the fraction of electrons in the j-th atom not involved in bonding and α_j the atomic polarizability of the j-th atom; and the basis for such calculation is the Lewis-Langmuir octet rule (1916) modified by Linnett (1961) as a double-quartet of electrons. Accordingly, each nitrogen in mercury dicyanide has only two valence electrons which are not involved in bonding while the other atoms have no valence electrons left unshared. Hence, $\Sigma\alpha_{\|n} = (4/5)\alpha_N = 5.944 \times 10^{-25}$ cm^3. The perpendicular component of a diatomic molecule is simply the sum of two atomic polarizabilities, i.e., $\alpha_\perp = 2\alpha_A$ for a nonpolar A_2 molecule and $\alpha_\perp = 2(X_A^2\alpha_A + X_B^2\alpha_B)/(X_A^2 + X_B^2)$ for an A B molecule where X refers to the electronegativity of the atom. Extending this to polyatomic molecule, the sum of all the perpendicular components is given as $\Sigma 2\alpha_\perp = n_{df}(\Sigma X_j^2\, \alpha_j)/(\Sigma X_j^2)$ where n_{df} is the number of residual atomic polarizability degrees of freedom. n_{df} is directly obtained from the configuration of a molecule and the assumption that each isolated atom possesses three polarizability degrees of freedom and every bond removes two of these three degrees of freedom with exception that (1) if two bonds are formed from the same atom and exist in a linear configuration, three atomic degrees of freedom are lost and (2) if three bonds are formed from the same atom and exist in a planar configuration, only five atomic degrees of freedom are lost. Accordingly, n_{df} is 5 for water, 6 for hydrogen cyanide, 7 for methane, 8 for acetylene, 9 for sulphur hexafluoride and 10 for mercury dicyanide (Fig. 1). Hence, $\Sigma\, 2\alpha_\perp = 277.851 \times 10^{-25}$ cm^3 for mercury dicyanide. The mean or average molecular polarizability is obtained in terms of the parallel bond, nonbond region electron and perpendicular bond contributions from the following expression : $\alpha_M = (1/3)(\Sigma\alpha_{\|b} + \Sigma\alpha_{\|n} + \Sigma 2\alpha_\perp)$. The calculated value of the molecular polarizability for mercury dicyanide is given as 145.331×10^{-25} cm^3.

Lippincott, Nagarajan and Stutman (1966) carried out the polarizability calculations for various polyatomic molecules and their values of bond parallel components in 10^{-25} cm^3 for the C ≡ N bond are 22.57 in cyanogen, 22.585 in methyl cyanide, 23.272 in methyl isocyanide and 23.183 in fluorine cyanide. These values are well comparable in magnitude with the one obtained here for the C ≡ N bond. Hence, the bond parallel components could be transferred from one one molecular system to another having similar chemical bonds with nearly identi-

cal internuclear distances. The small changes in the values of bond parallel components for the same bone appear above may be due to the slightly different values of the internuclear distances as the bond parallel component is roughly proportional to the fourth power of the internuclear distance. According to Lippincott, Nagarajan and Stutman (1966), the values of bond parallel components in 10^{-25} cm^3

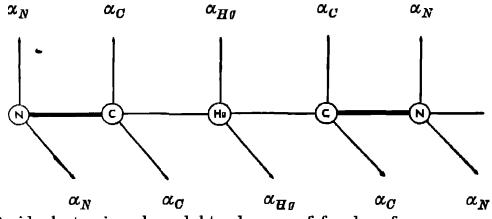

Fig 1. Residual atomic polarizability degrees of freedom for mercury dicyanide.

are 13.899 for the C—N bond in formamide and 18.937 for the C = N bond in hydrogen isocyanate and according to the present investigation it is 22 245 for the C ≡ N bond in mercury dicyanide The values, as is expected, are in the increasing order with the increase in bond order. The values of bond parallel components for the C—N multiple bonds are in the increasing order roughly in the ratio 14 . 19 : 22. If the π and σ electrons equally contribute to the bond parallel component, the values for the double and triple bonds should be twice and thrice the value for the single bond. Actually the contribution to the bond parallel component by the electrons occupied in the π-orbital is much less than that of the electrons occupied in the σ-orbital. The increment in the bond polarizability from the σ system to the $\sigma+\pi$ one is greater than that from the $\sigma+\pi$ system to the $\sigma+3\pi$ one. Refractive index for mercury dicyanide is not available either in the gaseous state or in the liquid state but in the crystalline form. Uniaxial crystals have two refractive indices, one of the rays vibrating parallel to the optic axis and another at right angles to this direction. If the extraordinary ray is greater than the ordinary one in a uniaxial substance, the substance is optically positive; if the reverse is true, negative. Uniaxial crystals may be considered simply as a small group of biaxial crystals which have three refractive indices, two lying in one plane and the third in another plane of the particle. These indices are identified by α, β, γ for the least, intermediate and the greatest index respectively of the substance If β is equal to α, the crystal is optically positive and to γ, negative. Since mercury dicyanide comes under this category and has a tetragonal system, it has two refractive indices The experimental values of these two refractive indices have been given by Lange (1952) and their values are 1.645 for the ordinary ray and 1.492 for the extra-ordinary ray. Using 252.646 as the molecular weight and 4 as the density, the molecular polarizability was calculated from the well-known Lorentz-Lorenz equation and its values are given as follows : 152.67×10^{-25} cm^3 for the ordinary ray and 95.121×10^{-25} cm^3 for the extraordinary ray. The calculated

value of molecular polarizability is in fairly good agreement with the experimental one for the ordinary ray.

ABSOLUTE RAMAN INTENSITIES OF Σ_g^+ MODES

One of the best applications of the relationships, namely, the R^3-dependence of the parallel component and the R-independent form of the perpendicular component of the polarizability in the neighbouring spectroscopic domains immediately appears to the evaluation of the absolute intensity of a Raman line which is proportional to $(\delta\alpha/\delta Q)^2$, the square of the change in the polarizability during a vibration. If one could obtain values for the internuclear separations before and after a vibrational transition, one would then be able to calculate the absolute intensity of a Raman line. To a first approximation from the delta-function potential model, only the bond parallel component need be considered to obtain $(\delta\alpha/\delta Q)$ through well defined transformation $(\delta\alpha/\delta R)$ where Q and R refer to normal mode and internuclear distance at the equilibrium configuration. It is aimed here to obtain $(\delta\alpha/\delta R)$ for the symmetrical stretching mode of a polyatomic molecule and then apply to the Σ_g^+ modes of oscillation in the ground electronic state of mercury dicyanide.

The polarizability derivative may be obtained by differentiating the analytical expression for the parallel component of the polarizability $\alpha_{\|\mu} = 4nA_{12}\sigma$

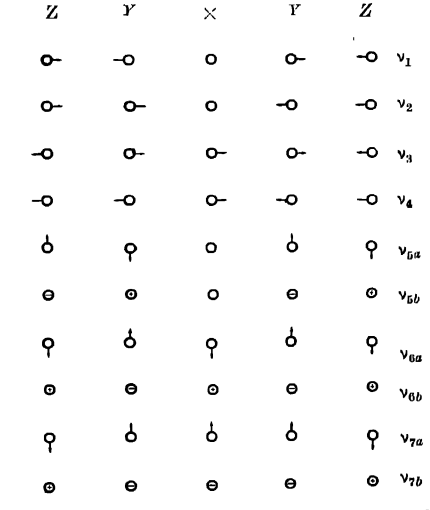

Fig. 2. Schematic representation of the normal modes of oscillation in a linear symmetrical $X(YZ)_2$ molecule. The positive signs designate the motions in the xz plane while the negative ones designate the same in the yz plane or vice versa.

$(1/a_0)(<x^2>)^2$ with respect to the internuclear distance R and neglecting terms of small magnitude and thus the obtained expression is given as $(\delta\alpha_{||_p}/\delta R) = nA_{12}\sigma(1/a_0)(R^3)$ Here only negligible errors have been introduced by assuming a contribution from only the leading term in the expression for $<x^2>$. The molecular polarizability of a diatomic molecule is generally written as a contribution from purely bond parallel and perpendicular components, i e., $\alpha_M = (1/3)(\alpha_{||_p}+2\alpha_\perp)$ The necessary desired quantity is the change in molecular polarizability due to the symmetrical stretching of the bond and in obtaining this, the following important features of the delta-function potential model have to be considered: Firstly, $(\delta\alpha_M/\delta R) = (1/3)(\delta\alpha_{||}/\delta R)$; in other words, the change is one-dimensional and secondly $(\delta\alpha_{||}/\delta R) = (\delta\alpha_{||_p}/\delta R)$; in other words, there is virtually no contribution from the nonbond region electrons. The quantity $(\delta\alpha_{||_p}/\delta R)^2$ is assumed to be directly proportional to the absolute Raman intensity of the stretching mode in the ground electronic state of a given molecule. Hence the analytical expression for the polarizability derivative with respect to the internuclear distance is given as follows .

$(\delta\alpha/\delta R) = (1/3)(\delta\alpha_{||}/\delta R) = (1/3)(\delta\alpha_{||_p}/\delta R) = nA_{12}\sigma(1/3a_0)(R^3)$ Since the delta-function potential model allows no interaction between neighboring bonds, the analytical expression described above is also applicable for a bond in a polyatomic molecule

Since the absolute intensities of Raman lines due to the symmetrical C N and Hg-- C stretching vibrations depend on the derivatives of the polarizabilities of the respective bonds, such calculations were made from the above equation using the internuclear distances, delta-function strengths, Bohr radius etc given earlier. The calculated values of the polarizability derivatides in Å^2 for the C $\equiv$ N and Hg—C bonds are 2.408 and 3.12, respectively. There is no experimental value of the polarizability derivative for the Hg—C bond but the C $\equiv$ N bond. The experimental value of the polarizability derivative 2 61 Å^2 reported by Chantry and Plane (1961) for the C $\equiv$ N bond in acetonitrile is in comparable magnitude with calculated one here and thus the polarizability derivatives are in general transferable, as in the cases of bond parallel components, from one molecular system to another having similar chemical bonds with nearly identical internuclear distances The bond region electrons are alone involved in the calculations of polarizability derivatives but the nonbond region electrons have no influence at all on the polarizability derivatives. The polarizability derivative is a dependent function of the internuclear distance as in the case of the bond parallel component of the polarizability but with third power.

MEAN AMPLITUDES OF VIBRATION

A molecule or ion of the $X(YZ)_2$ type possessing a linear symmetrical structure with the symmetry point group $D_{\infty h}$ gives rise, according to the relevant symmetry considerations and selection rules, to ten vibrational degrees of freedom consti-

tuting only seven fundamental frequencies which are distributed under the various irreducible representations as follows : $2\Sigma_g^+(R, p)+3\Sigma_u^+(I, \|)+\pi_g(R, dp)+2\pi_u(I, \perp)$ where R, I, p, dp, $\|$, and $\perp$ stand for Raman active, infrared active, polarized, depolarized, parallel and perpendicular, respectively; the subscript g represents the gerade modes which are symmetric with respect to the centre of symmetry while u the ungerade ones which are asymmetric with respect to the centre of symmetry The Σ type vibrations are the nondegenerate while the π type vibrations are the degenerate ones. The frequency ν_1 corresponds to the $Y - Z$ stretching vibration, ν_2 to the $X - Y$ symmetrical stretching vibration, ν_3 to the symmetrical $Y \equiv Z$ ssymmetrical stretching vibration, ν_4 to the $X-Y$ asymmetrical stretching vibration, ν_5 to the $X-\hat{Y}$ Z asymmetrical bending vibration ν_6 to the $X-\hat{Y} \equiv Z$ symmetrical bending vibration and ν_7 to the $Y-\hat{X}-Y$ symmetrical bending vibration A schematic representation of the normal modes of oscillation for a linear symmetrical molecule of $X(YZ)_2$ type has been given in Fig 2

Ten internal coordinates have been selected here to describe the ten vibrational degrees of freedom and they are given as follows : r_1 and r_2 are the $Y - Z$ stretching coordinates, d_1 and d_2 are the $X-Y$ stretching coordinates: θ_1 and θ_2 designate the $X - \hat{Y} \equiv Z$ bending coordinates in the xz plane while θ_1' and θ_2' designate the same in the yz plane; ϕ designates the $Y-\hat{X}-Y$ bending coordinate in the xz plane while ϕ' designates the same in the yz plane (see Fig 3) The

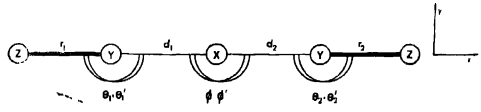

Fig 3. Geometric illustration of the internal coordinates for a linear symmetrical $X(YZ)_2$ molecule. The symbols denote the deviations from the values at the equilibrium configuration. θ and ϕ designate the changes of the $X-Y\equiv Z$ and $Y-X-Y$ angle bendings in the xz plane while θ' and ϕ' designate the same in the yz plane or vice versa. The equilibrium $X-Y$ and $Y\equiv Z$ internuclear distances are identified by the symbols D and R; respectively.

equilibrium internuclear distances $Y \equiv Z$ and $X-Y$ are being represented by the symbols R and D, respectively. On the basis of the principle postulated by Wilson (1939, 1941), a set of symmetry coordinates satisfying the conditions of normalization, orthogonality and transformations of the concerned irreducible representations has been constructed with help of the internal coordinates described above and given in the following :

$$S_1(\Sigma_g^+) = (2)^{-\frac{1}{2}}(r_1+r_2)$$

$$S_2(\Sigma_g^+) = (2)^{-\frac{1}{2}}(r_1-r_2)$$

$$S_3(\Sigma_u^+) = (2)^{-\frac{1}{2}}(d_1 - d_2)$$
$$S_4(\Sigma_u^+) = (2)^{-\frac{1}{2}}(\theta_1 - \theta_2)$$
$$S_{5a}(\pi_g) = RD(2)^{-\frac{1}{2}}(\theta_1' - \theta_2')$$
$$S_{5b}(\pi_g) = RD(2)^{-\frac{1}{2}}(\theta_1 + \theta_2)$$
$$S_{6a}(\pi_u) = RD(2)^{-\frac{1}{2}}(\theta_1 + \theta_2)$$
$$S_{6b}(\pi_u) = RD(2)^{-\frac{1}{2}}(\theta_1' + \theta_2')$$
$$S_{7a}(\pi_u) = D\phi$$
$$S_{7b}(\pi_u) = D\phi'$$

Here the angle displacements are multiplied by the equilibrium internuclear distances $R(Y - Z)$ and $D(X - Y)$ in order to keep the dimensions of the mean-square amplitude quantities referring to the angle bnding the same as those of the quantities due to the bonded atom pairs.

For a molecule or ion of the present study we will have sixteen mean-square amplitude quantities (σ) but the symmetry of the molecular or ionic system reduces to ten. The mean-square amplitude quantities due to the interaction between the bonded atom pairs and interbond angles are not at all permitted in this case as the parallel and perpendicular vibrations do not occur in the same symmetry species. Following the principle outlined by Cyvin (1959), the symmetrized mean-square amplitude matrices (Σ) in terms of the mean-square amplitude quantities (σ) have been obtained by introducing the symmetry coordinates as follows :

$$\Sigma_{11}(\Sigma_g^+) = \langle S_1^2 \rangle = \sigma_r + \sigma_{rr}$$
$$\Sigma_{22}(\Sigma_g^+) = \langle S_2^2 \rangle = \sigma_d + \sigma_{dd}$$
$$\Sigma_{12}(\Sigma_g^+) = \Sigma_{21}(\Sigma_g^+) = \langle S_1 S_2 \rangle = \sigma_{rd} + \sigma_{rd}$$
$$\Sigma_{33}(\Sigma_u^+) = \langle S_3^2 \rangle = \sigma_r - \sigma_{rr}$$
$$\Sigma_{44}(\Sigma_u^+) = \langle S_4^2 \rangle = \sigma_{dd} - \sigma_{dd}$$
$$\Sigma_{34}(\Sigma_u^+) = \Sigma_{43}(\Sigma_u^+) = \langle S_3 S_4 \rangle = \sigma_{rd} - \sigma_{rd}$$
$$\Sigma_{55}(\pi_g) = \langle S_{5a}^2 \rangle = \langle S_{5b}^2 \rangle = \sigma_\theta - \sigma_{\theta\theta}$$
$$\Sigma_{66}(\pi_u) = \langle S_{6a}^2 \rangle = \langle S_{6a}^2 \rangle = \sigma_\theta + \sigma_{\theta\theta}$$
$$\Sigma_{77}(\pi_u) = \langle S_{7a}^2 \rangle = \langle S_{7b}^2 \rangle = \sigma\phi$$
$$\Sigma_{67}(\pi_u) = \Sigma_{76}(\pi_u) = \langle S_{6a} S_{7a} \rangle = \langle S_{6b} S_{7b} \rangle = (2)^{\frac{1}{2}} \sigma_{\theta\phi}$$

where the entering quantities may be defined by the mean values given in the following :

$$\sigma_r = \langle r_1^2 \rangle = \langle r_2^2 \rangle$$
$$\sigma_{rr} = \langle r_1 r_2 \rangle$$
$$\sigma_d = \langle d_1^2 \rangle = \langle d_2^2 \rangle$$

$$\sigma_{dd} = \langle d_1 d_2 \rangle$$
$$\sigma_{rd} = \langle r_1 d_1 \rangle = \langle r_2 d_2 \rangle$$
$$\sigma_{rd} = \langle r_1 d_2 \rangle = \langle r_2 d_1 \rangle$$
$$\sigma_0 = RD\langle 0_1^2 \rangle = RD\langle 0_2^2 \rangle = RD\langle (\theta_1')^2 \rangle = RD\langle (0_2')^2 \rangle$$
$$\sigma_{\theta\theta} = RD\langle 0_1 0_2 \rangle = RD\langle \theta_1' \theta_2' \rangle$$
$$\sigma_\phi = D^2\langle \phi^2 \rangle = D^2\langle (\phi')^2 \rangle$$
$$\sigma_{0\phi} = (RD^3)^2\langle \theta_1 \phi \rangle = (RD^3)^2\langle 0_2 \phi \rangle = (RD^3)^2\langle 0_1'\phi' \rangle = (RD^3)^2\langle 0_2'\phi' \rangle$$

TABLE I

Fundamental frequencies in cm^{-1} and internuclear distances in Å in some linear dicyanides

Molecule or Ion	$\nu_1(\Sigma_g^+)$	$\nu_2(\Sigma_g^+)$	$\nu_3(\Sigma_u^+)$	$\nu_4(\Sigma_u^+)$	$\nu_5(\pi_g)$	$\nu_6(\pi_u)$	$\nu_7(\pi_u)$	$X-Y$	$Y-Z$
$Ag(CN)_2^-$	2141	360	2140	390	250	310	107	2.13	1.16
$Au(CN)_2^-$	2164	452	2141	427	304	368	100	2.10	1.16
$Hg(CN)_2$	2198	412	2194	442	276	341	100	2.20	1.15

The analytical expressions for the mean-square amplitudes of vibration for the nonbonded atom pairs may be obtained in terms of the symmetrized mean-square amplitude matrices as follows.

$$\sigma_{r+d} = \tfrac{1}{2}(\Sigma_{11}+\Sigma_{22}+\Sigma_{33}+\Sigma_{44})+\Sigma_{12}+\Sigma_{34}$$
$$\sigma_{r+2d} = \tfrac{1}{2}(\Sigma_{11}+4\Sigma_{22}+\Sigma_{33})+2\Sigma_{12}$$
$$\sigma_{2r+2d} = 2\Sigma_{11}+2\Sigma_{22}+4\Sigma_{12}$$
$$\sigma_{2d} = 2\Sigma_{22}$$

where σ_{r+d} is the mean-square amplitude quantity due to the nonbonded atom pair $Z-X$, σ_{r+2d} the quantity due to the nonbonded atom pair $Z-Y$, σ_{2r+2d} the quantity due to the nonbonded atom pair $Z-Z$ and σ_{2d} the quantity due to the nonbonded atom pair $Y-Y$.

On the basis of the principle postulated by Wilson (1939, 1941) and Fernglo and Meister (1951), the G matrix elements related to the kinetic energy were obtained in terms of the symmetry coordinates given above. In the analysis of the molecular vibrations, Cyvin (1959) was the first to introduce the symmetry coordinates in determining the mean-square amplitudes of vibration. According to his secular equation $|\Sigma G^{-1} - E\Delta| = 0$, the following equations for the normal frequencies containing the symmetrized mean-square amplitude matrices have been constructed under the various irreducible representations:

TABLE II

Symmetrized mean-square amplitude matrices in Å² in some linear dicyanides

Molecule or ion	Element	Symmetrized mean-square amplitude matrix	
		$T=298°K$	$T=500°K$
$Ag(CN)_2^-$	Σ_{11}	0 0038026	0 0061755
	Σ_{22}	0.0008223	0.0007461
	Σ_{33}	0.0043439	0.0067080
	Σ_{44}	0.0009400	0.0008846
	Σ_{55}	0 0252060	0.0392141
	Σ_{66}	0.0317268	0 0468469
	Σ_{77}	0 0145846	0 0201943
	Σ_{67}	0 0063895	0 0082748
$Au(CN)_2^-$	Σ_{11}	0 0019492	0 0036935
	Σ_{22}	0.0010494	0.0008205
	Σ_{33}	0.0031508	0 0050632
	Σ_{44}	0 0009583	0 0008516
	Σ_{55}	0 0146437	0 0220567
	Σ_{66}	0.0228695	0 0342683
	Σ_{77}	0 0113754	0.0164755
	Σ_{67}	0 0051476	0 0071886
$Hg(CN)_2$	Σ_{11}	0 0027272	0.0046519
	Σ_{22}	0.0009037	0.0007603
	Σ_{33}	0 0029152	0.0046504
	Σ_{44}	0 0009537	0.0008389
	Σ_{55}	0.0171536	0.0264093
	Σ_{66}	0.0259675	0.0383644
	Σ_{77}	0 0147568	0 0192256
	Σ_{67}	0 0069249	0 0086958

For the type Σ_g^+ vibrations :

$$\Delta_1+\Delta_2=[\Sigma_{11}+\Sigma_{22}(\mu_y+\mu_z)\mu_y^{-1}+2\Sigma_{12}]\mu_z^{-1}$$

$$\Delta_1\Delta_2=(\Sigma_{11}\Sigma_{22}-\Sigma_{12}^2)\mu_y^{-1}\mu_z^{-1}$$

TABLE III

Mean-square amplitude quantities in Å² in some linear dicyanides

Quantity	$Ag(CN)_2^-$		$Au(CN)_2^-$		$Hg(CN)_2$	
	T=298°K	T=500°K	T=298°K	T=500°K	T=298°K	T=500°K
σ_r	0.0040733	0.0064418	0.0025500	0.0043784	0.0028212	0.0046512
σ_{rr}	−0.0002707	−0.0002663	−0.0006008	−0.0006848	−0.0000940	0.0000008
σ_d	0.0008812	0.0008154	0.0010039	0.0008360	0.0009287	0.0007996
σ_{dd}	−0.0000589	−0.0000693	0.0000456	0.0000156	−0.0000250	−0.0000393
σ_v	0.0284664	0.0430305	0.0187566	0.0281625	0.0215606	0.0323869
σ_{vv}	0.0032604	0.0038164	0.0041129	0.0061058	0.0044070	0.0059776
σ_ϕ	0.0145846	0.0201943	0.0113754	0.0164755	0.0147568	0.0192256
$\sigma_{0\phi}$	0.0063895	0.0083748	0.0051476	0.0071886	0.0069249	0.0086958
σ_{2d}	0.0016446	0.0014922	0.0020988	0.0016410	0.0018074	0.0015206
σ_{r+d}	0.0049544	0.0072571	0.0035539	0.0052144	0.0037499	0.0054508
σ_{r+2d}	0.0057179	0.0079340	0.0040488	0.0060194	0.0046286	0.0061718
σ_{2r+2d}	0.0092498	0.0038432	0.0059972	0.0090280	0.0072618	0.0108244

For the type Σ_u^+ vibrations :

$$\Delta_3+\Delta_4 = \Sigma_{33}(2\mu_x+\mu_y)+\Sigma_{44}(\mu_y+\mu_z)+2\Sigma_{34}\mu_y(2\mu_x\mu_y+2\mu_x\mu_z+\mu_y\mu_z)^{-1}$$

$$\Delta_3\Delta_4 = (\Sigma_{33}\Sigma_{44}-\Sigma_{34}^2)(2\mu_x\mu_y+2\mu_x\mu_z+\mu_y\mu_z)^{-1}$$

For the type π_g vibration :

$$\Delta_5 = \Sigma_{55}[(\mu_z/R^2)+\mu_y\{(1/R)+(1/D)\}^2]^{-1}$$

For the type π_u vibrations :

$$\Delta_6+\Delta_7 = \Sigma_{66}K^{-1}+\Sigma_{77}L^{-1}+2\Sigma_{67}M^{-1}$$

$$\Delta_6\Delta_7 = (\Sigma_{66}\Sigma_{77}-\Sigma_{67}^2)[K^{-1}\ L^{-1}-(M^{-1})^2]$$

where μ_x, μ_y and μ_z are the reciprocal masses of the atoms X, Y and Z, respectively;

$K = \mu_z(1/R^2)+\mu_y\{(1/R)+(1/D)\}^2+2\mu_x(1/D^2)$; $L = 2(2\mu_y+\mu_y)(1/D^2)$ and
$M = -2[\mu_y(1/D)\{(1/R)+(1/D)\}+2\mu_x(1/D^2)]$.

In the above equations Δ has been related to the normal frequency ν as

$$\Delta_i = (h/8\pi^2\nu_i)\coth(h\nu_i/2kT)$$

where k is the Boltzmann constant and T the temperature in °K

The secular equations giving the normal frequencies in terms of the mean-square amplitude quantities were constructed with help of the vibrational and structural data given in Table I at the temperatures $T = 298°K$ and $T = 500°K$. The off-diagonal elements under the symmetry species Σ_g^+ and Σ_u^+ were neglected

TABLE IV

Mean amplitudes of vibration in Å in some linear dicyanides

Molecule or ion	Distance	Mean amplitude of vibration	
		$T=298°K$	$T=500°K$
$Ag(CN)_2^-$	C≡N	0.0638	0.0803
	Ag–C	0 0297	0 0286
	C - - - C	0.0406	0 0386
	Ag - - - N	0 0704	0 0852
	C - - - N	0.0756	0.0891
	N - - - N	0.0962	0.1177
$Au(CN)_2^-$	C≡N	0.0505	0 0662
	Au–C	0 0317	0 0289
	C - - - C	0.0458	0 0405
	Au - - - N	0.0596	0 0722
	C - - - N	0.0682	0 0776
	N - - - N	0.0774	0.0950
$Hg(CN)_2$	C≡N	0.0531	0.0682
	Hg–C	0.0305	0.0283
	C - - - C	0 0425	0.0390
	Hg - - - N	0 0612	0 0738
	C - - - C	0.0680	0.0786
	N - - - N	0.0852	0.1040

and only the diagonal elements Σ_{11}, Σ_{22} Σ_{33} and Σ_{44} were evaluated. Since the equation is singular under the species π_g, the symmetrized mean-square amplitude matrix Σ_{55} was directly evaluated. When the off-diagonal element was neglected under the species π_u, the equations resulted to imaginary values for the diagonal elements. Hence the off-diagonal element was taken into consideration and the symmetrized mean-square amplitude matrices Σ_{66}, Σ_{77} and Σ_{67} were evaluated in the manner described by Torkington (1949, 1951) The computed values of the symmetrized mean-sauare amplitude matrices in Å^2 for the three dicyanides are given in Table II at the temperatures $T = 298°$K and $T = 500°$K. The calculated values of the mean-square amplitude quantities in Å^2 are given in Table III at the two temperatures where σ_r is the mean-square amplitude quantity due to the bonded atom pair $Y \equiv Z$, σ_d the quantity due to the bonded atom pair $X-Y$,

σ_θ the quantity due to the bending $X-\hat{Y} \equiv Z$, σ_ϕ the quantity due to the bending $Y-\hat{X}-Y$ and σ_{rr} σ_{dd} and $\sigma_{\theta\phi}$ are the respective interaction quantities. The meaning of the quantities σ_{2d}, σ_{r+d} σ_{r+2} and σ_{2r+2d} has already been explained earlier. The corresponding calculated values of the mean amplitudes of vibration in Å for the bonded as well as nonbonded atom pairs are given in Table IV at the two temperatures for the three dicyanides. Since the interaction quantities between the bonded atom pairs and nonbonded atom pairs are not essential, they are not considered here.

The mean amplitude of vibration for the nonbonded atom pair, as is expected, is much greater than that of the bonded atom pair. The mean-square amplitude quantity due to the bending is in general several times greater than those of the bonded and nonbonded atom pairs The situation is exactly reversed in the cases of corresponding force constants The interaction quantities due to the bonded atom pairs are much smaller than that of the quantity due to the interaction of bendings. The mean-square amplitude quantities are in general in the increasing order with increasing temperature except for those due to the metal-carbon and carbon-carbon bonds. The mean amplitude of vibration for the metal-carbon bond is much smaller that that of the carbon-nitrogen bond Gold dicyanide ion is isoelectronic with mercury dicyanide. The atomic numbers of the central atoms are in the increasing order by one unit while those of the other atoms are fixed in the two systems. The obtained values of the mean amplitudes of vibration for the bonded as well as nonbonded atom pairs are in the increaing order, in contrast to the gaseous molecules and ions, from gold dicyanide ion to mercury dicyanide except for those due to the metal-carbon and carbon–carbon bonds This shows that the binding force between atoms is mercury dicyanide is greater than that in gold dicyanide ion. In the cases of gaseous molecules and ions the mean amplitudes of vibration will be in the increasing order when we go from a system with lower molecular or ionic weight to the one with higher molecular or ionic weight. In contrast to this, we observe a decrease in the values of mean amplitudes of vibration for the bonded and nonbonded atom pairs from silver dicyanide ion to gold dicyanide ion. This shows in the cases of crystals that the binding force between the atoms in a unit with higher molecular or ionic weight is less than that in the one with lower molecular or ionic weight irrespective of the nature (molecular or ionic) of the two systems concerned. Since experimental values of mean amplitudes of vibration for any of the systems studied here are not available, no comparison could be made at the moment with the results of the present study. However, the values of the present investigation would be very useful for the interpretation of electron diffraction studies in future. The values of the symmetrized mean-square amplitude matrices given in Table II would be readily considered in future for the computations of mean-square parallel amplitudes, mean-square perpendicular amplitudes and mean cross products in order to obtain the shrinkages of chemical bonds for these three systems.

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